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Anodic stripping voltammetry coupled with design of experiments for simultaneous determination of Zn^{+2}, Cu^{+2}, Pb^{+2}, and Cd^{+2} in gasoline

Jemmla M. Trindade [a,b], Lorena C. Martiniano [a,c], Vivia R.A. Gonçalves [c], Antonio G. Souza [a], Aldaléa L.B. Marques [c], Guintar L. Baugis [d], Teresa C.O. Fonseca [e], Chaojie Song [c], Jiujun Zhang [c], Edmar P. Marques [b,*]

[a] Pós-graduação em Química, CCEN-UFPB, João Pessoa, PB, Brazil
[b] Laboratório de Pesquisa em Química Analítica (LPQA), Departamento de Química, UFMA, São Luis, MA, Brazil
[c] Laboratório de Análises e Pesquisa em Química Analítica de Petróleo e Biocombustíveis (LAPQAP), Departamento de Tecnologia Química, UFMA, São Luis, MA, Brazil
[d] Petróleo Brasileiro S/A, Refinaria de Capuava – UN-RECAP, Av. Alberto Soares Sampaio, 2122-A, Parque Capuava, 09380-904 – Maua, SP, Brasil
[e] Centro de Pesquisa e Desenvolvimento Leopoldo Américo Miguêz de Mello, Diquim – CENPES / PETRÓLEO BRASILEIRO S/A – PETROBRAS Cidade Universitária, lha do Fundao, 21941-915 – Rio de Janeiro, RJ, Brasil

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ABSTRACT

In this paper a rapid method of anodic stripping voltammetry (ASV) coupled with experimental design was developed for simultaneous determination of Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} in gasoline samples. A microwave assisted gasoline digestion procedure for sample preparation was also established. The determination limit was found to be 0.24 μg L^{-1} for Zn^{2+}; 8.58×10^{-4} μg L^{-1} for Cd^{2+}; 0.13 μg L^{-1} for Pb^{2+}, and 0.87 μg L^{-1} for Cu^{2+}. It was found that the interferences of concomitant metal ions were negligible. Gasoline samples collected in the city of São Luis (MA), Brazil were analyzed using this developed method, and the results demonstrated that this method was reliable and accurate. It is expected that this method can be used as a routine technique for metal ion determination in gasoline.

1. Introduction

The presence of impurities such as metal ions in gasoline may cause performance degradation of internal combustion engines (ICEs) through fuel decomposition, precipitate formation, and parts corrosion [1,2]. Toxic fuel impurities are also a source of pollution in cities and in areas proximate to roads. In addition, the presence of such impurities, even in low concentrations, can lead to high fuel consumption.

In Brazil, ICE vehicles use a blended gasoline containing 22–25% alcohol (ethanol fuel). The blending process introduces a certain level of metal ions, such as Cu, Fe, Ni, and Zn. These metal ions can also be introduced during the processes of production, storage, and transportation. In addition to metal ions, other impurities such as organic sulfurs also exist in original oils and gasoline. In order to mitigate the degradation effects that impurities have on ICEs, as well as to reduce environmental pollution, it is necessary to determine and control the concentration of these impurities [3,4].

Currently, the most conventional technique to detect metals in petroleum and derivatives employs spectrometric measurements coupled with microwave-assisted oven digestion. However, using this technique one metal can be detected each time, and detection of multiple elements is problematic. Other techniques that could simultaneously detect multiple metal ions are expected.

Electroanalytical techniques are powerful tools for trace metal determination in the liquid phase. They have also demonstrated significant advantages in multicomponent analysis with high sensitivity [4,5] and selectivity [6]. Anodic stripping voltammetry (ASV), involving pre-concentration of the targeted metals, has a sensitivity of below parts-per-billion [5]. However, in order to reach such a high sensitivity, the experiment must be carefully designed and important experimental factors, which can affect both response and accuracy, need to be optimized. A well-designed experiment can provide signals with superior quality compared to those measured without optimization [7,8]. The most popular optimization process is "design of experiments" (DOE) [7]. In DOE, all experimental parameters are considered; the interaction between the factors is analyzed, and the main contributing factor is defined; how well the system/process performs in the presence of noise will also be answered. In addition, the use of DOE can significantly reduce the number of experiments required for a

* Corresponding author. Tel.: +55 98 2109 8299.
E-mail address: edmar@ufma.br (E.P. Marques).

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particular objective. So far, DOE has been successfully employed in the optimization of experimental variables in electroanalytical measurements [8,9].

In this work, we used ASV technique combined with DOE to determine trace levels of metals in gasoline. We carried out the DOE to optimize experimental conditions and variable interactions for electrochemical measurements of trace metals in gasoline. A procedure for the simultaneous determination of zinc, cadmium, lead, and copper concentration in a gasoline sample using stripping voltammetry was designed and validated. Reliable results with high levels of sensitivity were obtained. In addition, a wet digestion method using HNO_3–H_2O_2 in a closed system for gasoline samples was also developed.

2. Experimental

2.1. Reagents and solutions

Standard stock solutions (1000 mg L^{-1}) were purchased from Merck (atomic absorption spectrometric grade, Merck), were used to prepare solutions with diluted concentration. All other reagents were of analytical grade purity and used as received. High-purity de-ionized water was obtained from a Nanopure water system (NANOPURE Infinity, Barnstead model). Nitrogen gas (99.999%) was used to deaerate the testing solutions. Laboratory glassware was kept overnight in 10% (v/v) nitric acid solution and rinsed with deionized water before use.

In order to minimize potential contamination, preparation of all the solutions was performed in a clean room. Standard solutions of Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} were prepared by diluting the respective stock solutions with the high purity deionized water. The obtained solutions were stored in previously cleaned polyethylene bottles.

2.2. Instruments

Voltammetric measurements were carried out using a voltammeter (model BAS CV–50 W) with a hanging mercury drop electrode (HMDE) (model CGME–398). All experiments were conducted in a conventional electrochemical cell. An Ag/AgCl (3 M KCl) electrode, and a platinum wire were used as the reference electrode and auxiliary electrode respectively. The function of the auxiliary electrode is to complete the electric circuit. The solution pH was measured with a pH meter (DIGIMED model BMPH-PV). A microwave oven (Anton Paar model Microwave 3000) was used for digestion of gasoline samples.

2.3. Sampling and digestion

The gasoline samples were collected between January and February 2006 in different regions within the city of São Luis (MA), Brazil. The samples were digested in a mixture of HNO_3 and H_2O_2 with the assistance of microwave heating. Typically, an aliquot of 400 μL of gasoline sample (300 mg) was mixed with 4 mL of concentrated HNO_3 and 2 mL of H_2O_2. The mixture was then placed in the cavity Anton Paar – Multiwave 3000, equipped with a rotor four with weak quartz. The microwave power was ramped to 500 W in 2 min, and kept it for 15 min. Then the power was increased to 1000 W in 2 min, and held it for 20 min. In the heating processes, the ventilation of the oven was set at level 1. After that, the microwave was shut down, the mixture was kept in the oven for 5 min with a ventilation set at level 3. The heating program is shown in Table 1 [10]. After digestion, the solution was diluted to 25 mL with ultrapure deionized water, which was used for electrochemical measurement. Two duplicated digestions were performed for each sample.

Table 1
Focused microwave-assisted oven heating program for gasoline samples.[a]

Step	Ramp (min)	Hold (min)	Power (W)	Fan
1	2	15	500	1
2	2	20	1000	1
3		5	0	3

[a] Program of heating based on previously published work [11].

2.4. Voltammetric procedure

The testing solutions prepared as follows: an aliquot of 5 mL of the digested solution (digested and diluted) was transferred into the electrochemical cell and the final pH of the solution was adjusted to a desired value by the addition of NH_4OH solution. All solutions were purged with N_2 for 15 min before ASV measurements. During the measurements, the solution was under constant stirring and bubbled with nitrogen gas. The HMDE was held at −1100 mV (vs. Ag/AgCl) for 120 s to electrodeposit zinc, cadmium, lead, and copper on the HMDE. After 10 s of quiescence, the electrode was scanned from −1000 mV to 125 mV at a scan rate of 20 mV s^{-1} to record the voltammogram. A pulse amplitude of 25 mV with 1 μA V^{-1} sensitivity was applied during this stripping scanning. Each experiment was repeated twice with a new HDME.

2.5. Design of experiments

The optimization process was carried out using a two-level factorial design [11,12]. In a typical experimental design, the experiment number (N) was calculated by the expression $N = 2^k$, where k is the number of variables. Solution pH, electrodeposition potential (E_{ed}), and electrodeposition time were the variables studied. Since electrodeposition time is a weak variable compared to the other two once it was held long enough, we did the factorial design using pH and E_{ed} as two variables to get optimal pH and electrodeposition potential, while kept the electrodeposition time fixed. Once the optimal pH and electrodeposition potential were found, the optimal electrodeposition time was then selected under these optimal conditions.

Prior to the DOE experiments, a set of preliminary experiments was performed to obtain critical variable ranges. Maximum and minimum values of each factor were established according to the results. All the experiments were carried out in a random order and repeated.

Statistical analysis was performed using Statistic 7.0 for the experimental design and to generate the response surface.

The standard addition method (ASV current vs. metal ion concentration) was used to determine each trace metal concentration. The slope of the ASV current vs. metal concentration curve was used to calculate the metal ion concentration in the sample solution and in the blank. The difference between the metal concentrations in sample and blank solutions gave the real metal concentration in the digested solution, from which the real metal concentration in the gasoline sample was calculated.

2.6. Graphite furnace atomic absorption spectrometry (GFAAS) measurements for metal concentrations

Metal concentrations in the digested samples were also measured using GFAAS. The parameters used for Zn^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+} in GFAAS are listed in Table 2.

Table 2
Operation and heating program parameters for GFAAS.

Spectrometer setup				
	Zn	Cd	Pb	Cu
λ (run)	213.9	228.8	217.0	324.8
Band pass (nm)	1.0	0.5	0.5	0.5
Lamp type	HCl[a]	HCl[a]	HCl[a]	HCl[a]
Lamp current (Ma)	1.0	4.0	10.0	4.0
Heating program for the atomizer				
Step	Step temperature (°C)		Time (s)	Argon flow rate (mL min^{-1})
Drying 1	85		5.0	3,0
Drying 2	95		40.0	3.0
Drying 3	120		10.0	3.0
Pyrolysis	300^{Zn}; 250^{Cd};$S00^{Cu}$;400^{Pb}		8.0	3.0
Atomization	1900^{Zn}; 1800^{Cd}; $23OO^{Cu}$; 2100^{Pb}		4.8	0.0
Cleaning	1900^{Zn}; 1800^{Cd}; 2300^{Cu}; 2100^{Pb}		2.0	3.0

[a] HCl Hollow cathode lamp.

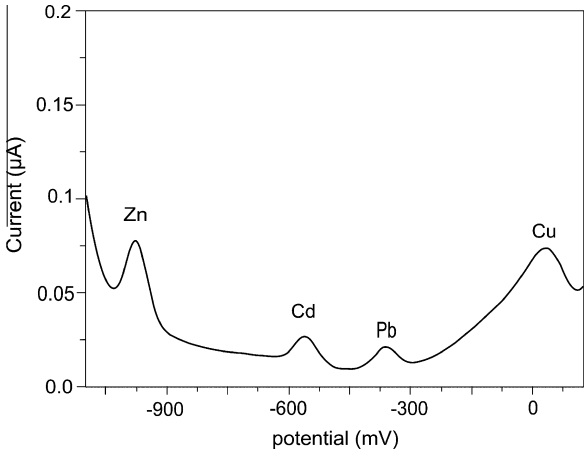

Fig. 1. Voltammogram at HMDE for a digested gasoline sample solution in an electrochemical cell containing 50 nmol L^{-1} of Zn^{+2}, 5 nmol L^{-1} of Cd^{+2}, 50 nmol L^{-1} of Pb^{+2}, and 1.25 nmol L^{-1} of Cu^{+}. Electrodeposition time: 120 s; electrodeposition potential: −1100 mV; pulse amplitude: 50 mV; potential scan rate: 25 mV s^{-1}; and pH: 1.2.

Table 3
Factors and levels used in the factorial design.

Variable	(−)	(+)	(0)
Zn^{+2}, Cd^{+2}, Cu^{+2}, and Pb^{+2}			
E_{ed}(mV) pH	−1300 1.0	−1100 5.0	−1200 3.0

E_{ed} = electrodeposition potential.

Table 4
Results of 2^2 experimental design for experimental variable optimization in a digested gasoline sample solution determined by anodic stripping voltammetry (ASV).

pH	$-E_{ed}$(mV)	Current (nA)			
		Zn^{+2}	Cd^{+2}	Pb^{+2}	Cu^{+2}
1.0	1300	160	89.9	22.0	37.5
5.0	1100	60	79.9	39.1	68.4
1.0	1100	215	95.7	27 2	31.0
5.0	1300	82	78.5	36.2	ND
3.0	1200	150	80.0	25.0	30.0

t_d = 120 s; E_{ed} = electrodeposition potential; ND = not detected.

3. Results and discussion

3.1. Response of ASV in the presence of metal ions

Fig. 1 shows a typical anodic stripping voltammogram for a digested gasoline solution. The peak currents corresponding to these four target ions can be clearly observed at −976 mV for Zn^{2+}, −560 mV for Cd^{2+}, −360 mV for Pb^{2+}, and 40 mV for Cu^{2+}. The peak current (i_p) was used as the response to optimize the experimental parameters.

3.2. Optimization of experimental parameters using factorial design

Optimization of measurement conditions is usually based on an experiment designed to characterize the importance and combined effects of the main experimental variables. In this work, the experimental design was operated in a typical 2^2 factorial pattern with two variables (pH and E_{ed}) and one response (peak current (i_p), evaluated at two levels (maximum and minimum) for a total of four independent experiments. The electrodeposition time (t_d) was kept at 120 s, which is long enough to get significant response. Table 3 lists the values corresponding to the maximum (+), minimum (−) and center point (0). Table 4 shows the results obtained from this experimental design.

A Pareto chart was constructed, as shown in Fig. 2. Bar lengths in Fig. 2 are proportional to the absolute value of the estimated effects, which help in determining the importance of relative effects. By variance analysis of these experimental data, it can be seen that: (1) pH is a significant factor for Cd^{2+}, Pb^{2+}, and Zn^{2+}, but it is not for Cu^{2+}, (2) E_{ed} is less significant than pH for all the four ions, and (3) the interaction between pH and E_{ed} is only statistically significant for Cd^{2+} and Cu^{2+}, especially for Cu^{2+}. Thus pH is the significant factor for all the four ions.

Three-dimensional (3D) response surface figure were also plotted for the four targeted metal ions. The relationship between i_p, E_{ed}, pH, is shown in Fig. 3. For Cu^{2+} (Fig. 3a), there is a valley range, suggesting that in order to achieve a high current, the measurement must be carried out at high pH and low E_{ed}. For Pb^{2+}, a maximum current could be obtained at a minimum level of E_{ed} and a maximum pH level. For Cd^{2+} (Fig. 3c), the E_{ed} has no significant effect on the current response, and low pH could help in obtaining a maximum current response; similar behavior was obtained for Zn^{2+} (Fig. 3d). Based on the observations and discussion above, the optimal conditions are pH = 1.0 and E_{ed} = −1100 mV.

In the analysis shown in Figs. 2 and 3, the optimum values for electrodeposition potential and solution pH were obtained. However, the electrodeposition time can also affect the current response. To find the optimum electrodeposition times, the peak

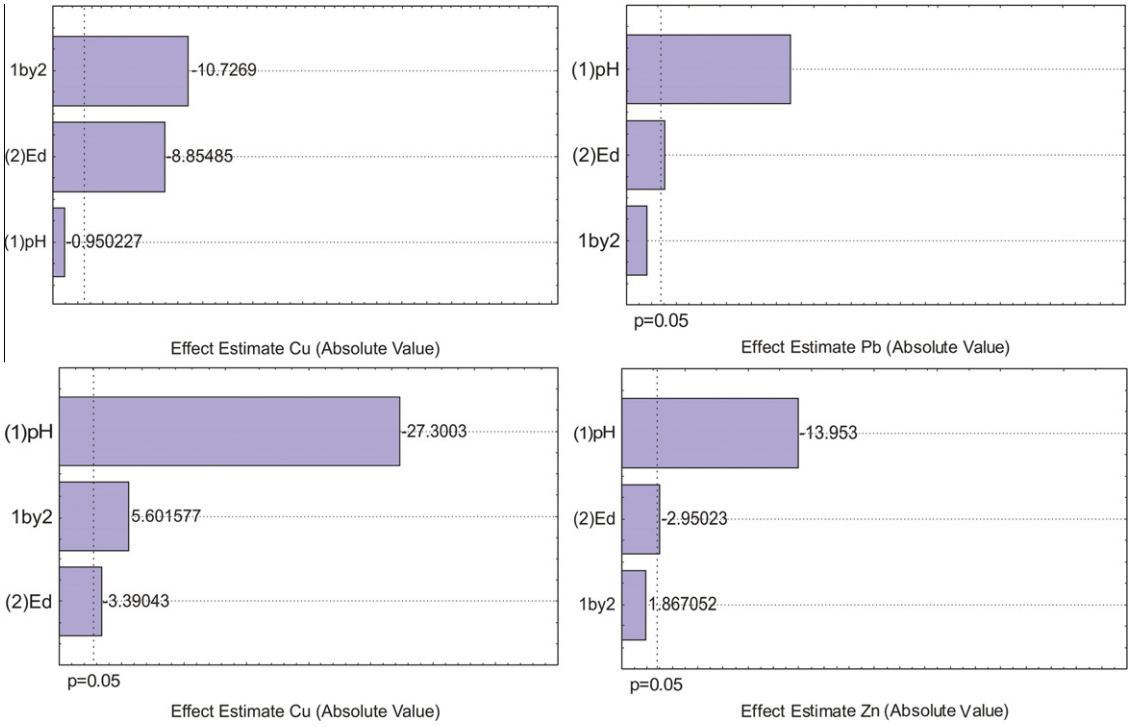

Fig. 2. Pareto chart of the variable effects based on the data in Table 4.

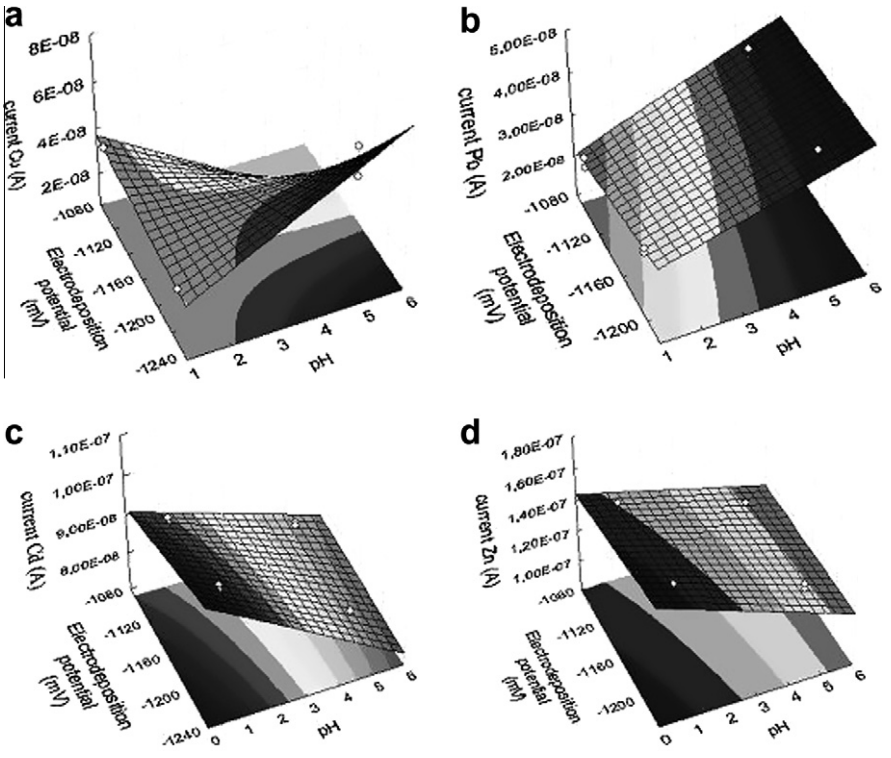

Fig. 3. Response surface for the 2^2 factorial designs in the optimization of measurement variables (electrodeposition potential and pH), measured in a digested gasoline sample solution by ASV. a: Cu^{2+}; b: Pb^{2+}; c: Cd^{2+}; and d: Zn^{2+}.

currents for all metal ions in the sample solution were also measured as a function of electrodeposition time using the optimized experimental conditions. Fig. 4 shows the typical results for the four metal ions. For Zn^{2+}, the peak current increases with increasing electrodeposition time before 120 s and after that it reaches a plateau. For Pb^{2+}, a slight increase in current response with increasing electrodeposition time can be observed. However, for both Cu^{2+} and Cd^{2+}, the electrodeposition time seems to have no

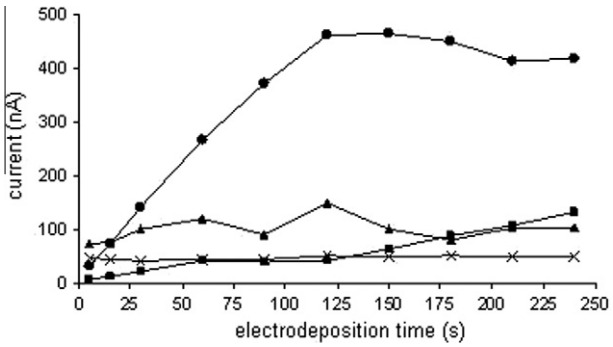

Fig. 4. Effect of electrodeposition time on current response measured by ASV for: (●) zinc; (▲) copper; (■) lead; and (x) cadmium, using a digested gasoline sample solution.

effect on the current response. Thus 120 s is an optimum electrodeposition time for the simultaneous detection of the four ions. Table 5 lists these optimum parameters.

Table 5
Optimized parameters for the determination of Zn^{+2}, Cd^{+2}, Pb^{+2}, and Cu^{+2} in the digested gasoline sample solutions, measured by ASV.

Electrodeposition time	120 s
Equilibrium time	10 s
Electrodeposition potential	−1100 mV
Scan rate	25 mV s^{-1}
Pulse amplitude	50 mV
Pulse period	200 s
pH	1.0

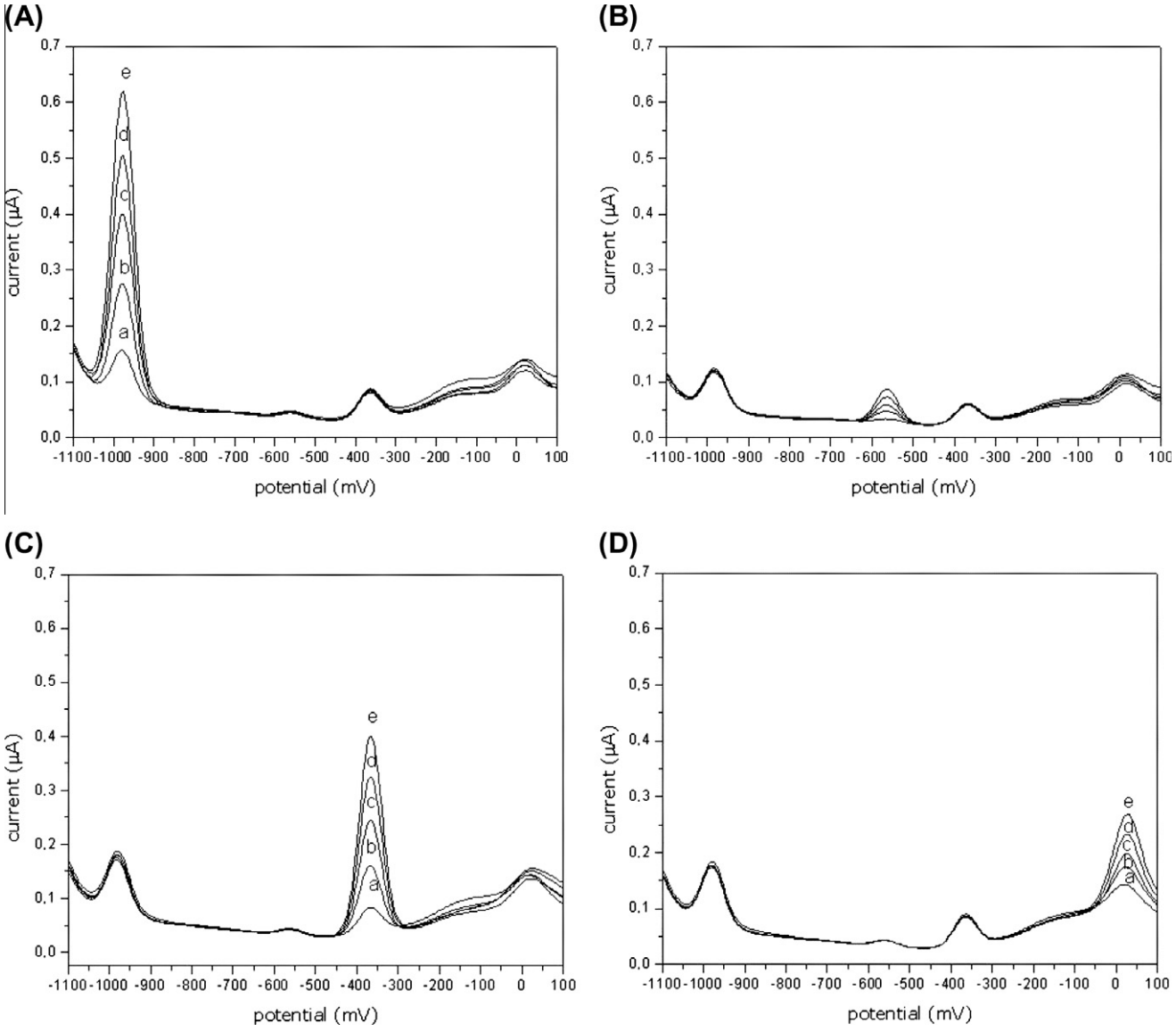

Fig. 5. Voltammograms at HMDE for gasoline digested sample solutions. Electrodeposition time: 120 s; electrodeposition potential: −1100 mV; pulse amplitude: 50 mV; scan rate: 25 mV s^{-1}; pH: 1.2. Voltammetric conditions: (A) Zn^{+2} in the presence of 0.01 nmol L^{-1} of Cd^{+2}; 0.125 nmol L^{-1} of Pb^{+2} and 0.025 nmol L^{-1} of Cu^{+2} under optimized conditions with successive additions of Zn^{+2}: (a) 0.25 nmol L^{-1}, (b) 0.05, (c) 0.10, (d) 0.15, and (e) 0.20 mmol L^{-1}. (B) Cd^{+2} in the presence of 0.25 nmol L^{-1} of Zn^{+2}, 0.125 nmol L^{-1} of Pb^{+2}, and 0.025 nmol L^{-1} of Cu^{+2} under optimized conditions with successive additions of Cd^{+2}: (a) 0.01 nmol L^{-1}, (b) 5.0, (c) 10.0, (d) 15.0, and (e) 20.0 nmol L^{-1}. (C) Pb^{+2} in the presence of 0.25 nmol L^{-1} of Zn^{+2}, 0.01 nmol L^{-1} of Cd^{+2}, and 0.025 nmol L^{-1} of Cu^{+2} under optimized conditions with successive additions of Pb^{+2}: (a) 0.025 nmol L^{-1}, (b) 25.0, (c) 50.0, (d) 75.0, and (e) 100.0 nmol L^{-1}. (D) Cu^{+2} in the presence of 0.25 nmol L^{-1} of Zn^{+2}, 0.01 nmol L^{-1} of Cd^{+2}, and 0.125 nmol L^{-1} of Pb^{+2} under optimized conditions with successive additions of Cu^{+2}: (a) 0.025 nmol L^{-1}, (b) 0.125, (c) 0.250, (d) 0.375, and (e) 0.500 nmol L^{-1}.

Table 6
Figures of merit of calibration curves against gasoline sample.

Analyte	Range (nmol L^{-1})	Equation curve	Linearity R^2	LOD (nmol L^{-1})	LOQ (nmol L^{-1})
Zn^{+2}	7.89–31.50	$Y = 5.13 \times 10^{-9} + 2.41 \times 10^{-9}X$	0.999	1.12	3.72
Cd^{+2}	4.44–17.70	$Y = 4.15 \times 10^{-10} + 2.94 \times 10^{-9}X$	0.999	2.29×10^{-3}	7.64×10^{-3}
Pb^{+2}	12.0–48.20	$Y = 7.17 \times 10^{-9} + 2.62 \times 10^{-9}X$	0.998	0.183	0.61
Cu^{+2}	15.30–61.20	$Y = 8.85 \times 10^{-9} + 4.64 \times 10^{-9}X$	0.997	4.11	1.37

Table 7
Concentrations of Zn^{+2}, Cd^{+2}, Pb^{+2}, and Cu^{+2}, using the calibration curves obtained by the method developed in this work and the GFAAS method, in gasoline samples digested in HNO_3–H_2O_2 mixture.

	ASV (mol L^{-1})	GFAAS (mol L^{-1})
Analyte	$X \pm st/\sqrt{n}$	
Zn^{+2}	$4.26 \times 10^{-7} \pm 0.70 \times 10^{-7}$	4.22×10^{-7}
Cd^{+2}	$2.82 \times 10^{-8} \pm 0.10 \times 10^{-8}$	2.73×10^{-8}
Pb^{+2}	$5.47 \times 10^{-7} \pm 0.04 \times 10^{-7}$	5.68×10^{-7}
Cu^{+2}	$3.81 \times 10^{-9} \pm 0.03 \times 10^{-7}$	3.91×10^{-7}

X: Average value ($n = 3$); t: student's t ($P < 0.05$).
s: Estimation of the standard deviation, n: number of determinations.

Table 8
Recovery values for the spiked samples (evaluation of the sample preparation).

	Concentration ($n = 3$)		
Analyte	Spiked (μmol L^{-1})	Recovery (μmol L^{-1})	Recovery (%)
Zn^{+2}	1.14	1.13	99.8
Cd^{+2}	2.33	2.31	99.1
Pb^{+2}	3.70	3.87	104.8
Cu^{+2}	6.00	6.60	110.1

3.3. Interferences

Possible interferences from concomitant metal ions were also investigated in this work. Fig. 5A–D shows the peak current changes vs. target ion concentration for Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} respectively, while keeping the other three ions concentration constant. All four cases show that changing the concentration of the targeted metal ion does not significantly affect the other three metals' current responses, suggesting that the interference from these concomitant metal ions is negligible. Therefore, simultaneous determination of Zn^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} using standard addition method is possible. The slopes of the calibration curves thus obtained were not significantly different from that of the calibration curves obtained in the absence of the other metals.

3.4. Applications

The method developed in this work was used to simultaneously determine the concentration of cadmium, lead, copper, and zinc in gasoline samples collected in the city of São Luis (MA), Brazil. Using the established experimental conditions, the following performance data were obtained: linearity and linear range, precision limit of detection (LOD), limit of quantization (LOQ), and accuracy. The LOD was calculated according to Miller and Miller's description [13],

$$\mathrm{LOD} = k\sigma/m \quad (1)$$

where $k = 3$, σ is the standard deviation of three measured blank samples, and m is the slope of the calibration graph. The LOQ was also calculated using Eq. (1) with $k = 10$. The results are presented in Table 6.

In Table 6, the linearity and linear range were obtained through triplicate analysis from a calibration graph with five concentration levels. The measurements were conducted using an electrodeposition time of 120 s at −1100 mV. For 5 mL of digested gasoline sample, the determination limit was found to be 0.24 μg L^{-1} for zinc, 8.58×10^{-4} μg L^{-1} for cadmium, 0.13 L^{-1} for lead, and 0.87 μg L^{-1} for copper.

The measurement accuracy of this method was evaluated by comparing the data to those obtained using the GFAAS technique. The results, listed in Table 7, show a good agreement between these two techniques. A recovery study was also performed to evaluate the reliability of the sample preparation process developed in this work. Table 8 summarized the recovery results. The recovery range of 99–110% demonstrates the reliability of the method developed in this work. These results showed that a reliable, accurate method was developed, which can be used in other labs for the detection of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} ions in gasoline samples.

4. Conclusions

A method of anodic stripping voltammogram coupled with design of experiments was developed in this paper for simultaneous determination of lead (II), zinc (II), copper (II), and cadmium (II) in gasoline samples. In addition, a gasoline digestion procedure assisted by microwave oven was also established. The measurement results demonstrated that this method was sensitive, convenient, and reliable. Interference from concomitant metal ions was also tested, and the obtained results showed that in each case the interference was insignificant. The determination limit was found to be 0.24 μg L^{-1} for zinc, 8.58×10^{-4} μg L^{-1} for cadmium, 0.13 μg L^{-1} for lead, and 0.87 μg L^{-1} for copper.

Gasoline samples collected in the city of São Luis (MA), Brazil were analyzed using the method developed, and the results demonstrated the measurements were reliable and accurate. It is anticipated that this method can be used as a routine tool for metal ion determination in gasoline.

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